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EFFECT OF UNIAXIAL PRESSURE ON THE FERROELECTRIC PHASE TRANSITION OF DTGS

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The effect of uniaxial pressure on hysteresis loops of DTGS single crystals was investigated up to 1 kbar, approximately. The coefficients $\gamma_i \equiv \delta T_c/\delta X_i$ for the X, Y and Z directions are established, and are equal to -3.5, -8.2 and 12.7 °C/kbar, respectively. It has been found that the coefficient of the fourth power, ξ, is not pressure and temperature dependent. A scaled representation of data $P/(|1-X/X_c|)^{1/2}$ vs $E/(|1-X/X_c|)^{3/2}$ shows typical Landau behaviour analogous to that of an ordinary phase transition with P= P(E,X) instead of P= P(E,T).

It is well known that an external pressure affecting intermolecular interactions changes many physical properties of crystals. Specially in ferroelectrics, pressure (X), as third independent field together with temperature T and electric field E, gives a unique possibility for the experimental study of their critical behaviour[1].

The influence of hydrostatic pressure on physical properties of TGS single crystals, as well as on its isomorphous selenate (TGSe) and fluoroberylate (TGFB) crystals, has been studied by several authors and is well described[2]. A pronounced effect of hydrostatic pressure is observed in TGSe crystals, which shows the triple point at 49 °C and 7.35 kbar[3], and suggests a tricritical point (TCP) at ≃40.6 °C and ≃5 kbar[4]. Very recently, the effect of hydrostatic pressure on phase transition of DTGS with different degree of deuterization has been reported by Yushu et al.[5]

Within the family of TGS type crystals, effects of two-dimensional pressure studies have been performed only in TGS[6]. The results obtained agree with the predictions of the phenomenolo- gical theory as well as with Janovec's theory.

The behaviour of dielectric constant ε_b of TGS as a function of uniaxial pressure applied along the x,y and z-axis up to 600 bar was first investigated by Imai[7]. Stankowska et al.[8] extended these studies to TGS, TGSe and TGFB crystals in several coordinate systems. Agreement between the coefficients $\gamma_i \equiv \partial T_c/\partial X_i$ for TGS in the system of Konstantinova[9] given by Imai and by Stankowska et al. is excellent. The linear shift of T_c for all axis were found, and the values of the three rates combine to reproduce fairly well the value given by hydrostatic and two-dimensional pressure. Also agreement with the fenomenological and Janovec's theories, as well as with Ehrenfest relation, was obtained. Recently Brillouin studies[10], acoustic properties on TGS crystals[11] under moderate uniaxial stress (X∥b) and studies of the behaviour of hysteresis loops of TGS under variable uniaxial stress (X∥a,b,c*)[12] have been reported.

Deuterated crystals of TGS have not been the subject of study under the influence of anisotropic pressure. Very recent studies[13] of quadrupole interactions in ferroelectrics of the TGS family indicate possible existence of TCP in deuterated crystals (DTGS) of that family and suggest that it may be induced by uniaxial pressure.

The aim of this paper is to give experimental evidence (if any) of the existence of a TCP in DTGS as well as characterization of the phase transition under uniaxial pressure with X as an independent variable (similar to T).

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DTGS crystals used by us in the present measurements were, some grown for us by Cleveland Crystals Inc., some grown and donated by Prof. Stankowska (Adam Mickiewicz University). The degree of deuteration was stablished as about 90% using the relation between T_c and deuteration content in this type of crystals given by Brezina and Smutny[14] and recently by Yushu et al.[5] The samples were small parallelepipeds approximately 2x5x5 mm^3. Gold leaf electrodes were attached on each b face.The coordination system used by us is XYZ (or abc*) which are commonly used in ESR studies (see Stankowska et al.[8]). Spontaneous polarization was measured by the use of a Sawyer-Tower circuit and a digital oscilloscope (Nicolet-310). The temperature was measured by a chromel-alumen thermocouple attached directly to the sample with an accuracy of $\pm 0.02^{o}C$. The sample holder was inserted in a thick metal tube and then immersed in an oil bath. The temperature of the bath was controlled by a temperature controller (Haake F-3). In this way we achieved thermal stability better than $\pm 0.02^{o}C$ in the period of time necessary for isothermal measurements of spontaneous polarization. During isobaric measurements of P_s, spontaneous cooling with rate $1^{o}C$/hour or less was used. A known force was applied to the sample through the modified version of a simple mechanical set-up[12] .We found that depending on the perfection of the samples used, we could avoid cracking by uniaxial pressure up to ≈1kbar.

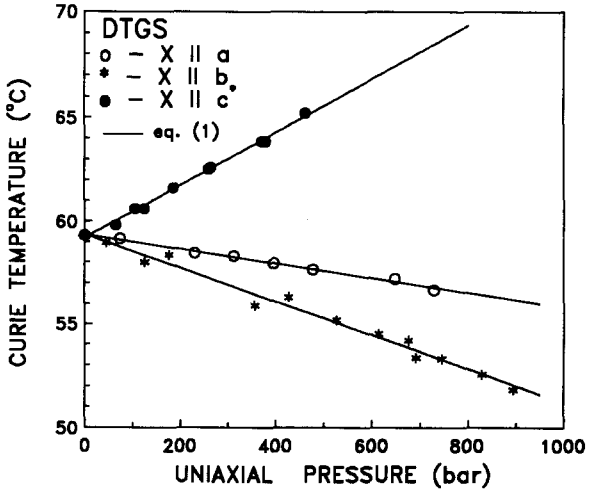

Fig. 1 Curie temperature T_c as a function of uniaxial pressure applied to the directions X, Y, Z (a, b, c*) of DTGS single crystal.

The transition temperature was obtained from the plot of squared spontaneous polarization P_s as a function of temperature T for different values of the uniaxial pressure applied parallel to X, Y or Z directions. The shifts of T_c are shown in Fig. 1, and it can be seen that within the limit of experimental error the dependence of T_c on uniaxial pressure is linear for all axis. The rate of increase of the transition temperature T_c with uniaxial pressure can be written in the form:

$$T_c = T_c^o + \gamma_i X_i \qquad (1)$$

where T_c^o is the transition temperature at atmospheric pressure, $T_c^o = 59.3\ ^{o}C$.

The coefficients $\gamma_i \equiv \partial T_c/\partial X_i$ were obtained as the best fit of experimental points and they are equal to -3.5 ± 0.3 for X (a) axis, -8.2 ± 0.7 for the Y (b) axis and 12.7 ± 0.9 for Z (c*) axis, all in units of ^{o}C/kbar. The sum $\sum \gamma_i$ of shift for the three axes is equal to $1 \pm 1.7\ ^{o}C$/Kbar. This value is in good agreement with the rate of $2.6\ ^{o}C$/Kbar for hydrostatic pressure[5] taking into account the experimental error.

Because of the lack of thermal expansion as well as electrostiction coefficient data for DTGS ,direct comparison with Ehrenfest relation or fenomenological theories can not be done at present . However, one may expected much higher changes of the above mentioned coefficients at T_c,as was found for specific heat[15].

Our measurements show that P_s in the vicinity of the transition temperature is well described by:

$$P_s^2 = -(4\pi/C\xi)\ [T-(T_c^o + \gamma_i X_i)] \qquad (2)$$

where C is the Curie constant and ξ is the coefficient of the P^4 terms in the free energy expansion equation [see Ref. 1]. Taking into account that $C = 2550\ ^{o}K$[16] we obtained $\xi = (16.4 \pm 0.9)\times 10^{-10}$(esu) which is in very good agreement with the value previously reported[15,17]. We found that ξ is independent on uniaxial pressure, with a limit for the experimental errors of ±5% for the three directions studied up to 1 kbar. It means that for moderate uniaxial pressure the TCP behaviour for DTGS can not be observed.

For several fixed temperatures we studied the P_s behaviour as a function of uniaxial pressure.In the vicinity of X_c, P_s^2 is linear and does not depend on temperature. So similar relation to (2)

holds in that case. In his way we could confirm a purely stress induced continuous (second order) transition in DTGS single crystals. $(X-X_c)$ at fixed temperature plays the same role as $(T-T_c)$ at fixed stress in the ordinary phase transition (usually X≡ atmospheric pressure). The analogy with the ordinary phase transition suggests that the results could be analyzed using scaled variables:

$$p \equiv \hat{P}/(|1-X/X_c|)^{1/2}$$

and

$$e \equiv \hat{E}/(|1-X/X_c|)^{3/2} \quad ,$$

with $\hat{P} = P/P_{so}$, $\hat{E} = E/E_o$, where E_o and P_{so} are the saturation internal field and the saturation polarization, respectively.

This leads to an equation of state of the type:

$$e_{\pm} = ap(bp^2 \pm 1) \qquad (3)$$

where e_- corresponds to $X<X_c$ and e_+ to $X>X_c$ and coefficients a and b appearing in eq. (3) are not stress dependent. Introducing these proportionality factors is equivalent to the renormalization of the saturation value of E_o and P_{so}. The best fit of the experimental data is obtained with $a = 7.0\times10^{-5}$ and b = 30.6. Figure 2 shows a plot of mean field equation of state in the scaling form, along with the experimental data for the temperature $T= T_c^o - 0.42\ ^oC$, i.e, $X_c= 50$ bar, with uniaxial pressure applied parallel to Y axis. Good data collapsing at critical pressure is observed in the same fashion as it was seen for ordinary phase transition of TGS type crystals[1].

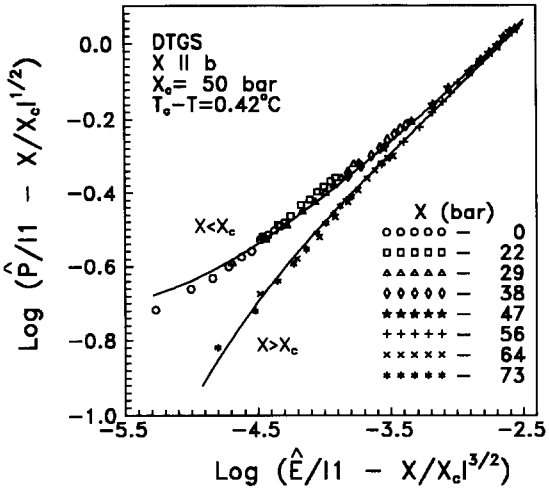

Fig. 2 Log-Log plot of scaled polarization versus scaled electric field for ferroelectric DTGS. Full line is renormalized mean-field equation of state.

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References

1. J.A.Gonzalo "Effective Field Approach to Phase Transition and Some Applications to Ferroelectrics", World Scientific, Singapore 1991.
2. J. Stankowski, A. Galezewski, S. Waplak, U.Gruszczynska and H.Gierszal, Ferroelectrics 6, 209 (1974), and references therein.
3. K. Gesi and K. Ozawa, J. Phys. Soc. Jpn. 37, 1053 (1974), and references therein.
4. H. Yamashita, Y. Takenchi and J. Tatsuzaki, J. Phys. Soc. Jpn. 49, 1874 (1980).
5. Y. Yushu, L. Fenying, L. Xueshi, Z. Zhengrong and W. Min, Ferroelectrics 101, 267 (1990).
6. K. Mori and M. Mayashi, J. Phys. Soc. Jpn. 33, 1396 (1972).
7. K. Imai, J. Phys. Soc. Jpn. 36, 1069 (1974).
8. J. Stankowska,J. Polowinko and J. Stankowski, Ferroelectrics 21, 529 (1978).
9. U.P. Konstantinova, E.M. Silvestrova and K.S. Aleksandrov, Kristallografiya 4, 69 (1959).
10. R. Ramirez, C. Prieto and J.A. Gonzalo, Ferroelectrics 100, 181 (1989).
11. A.E. Dvornikova and O. Yu Serdobol'kaya, Sov.Phys. Sol.Stat. 31, 672 (1989).
12. M.F. Lapeña, R. Ramirez, J.A. Gonzalo and M. Koralewski, Ferroelectrics 125, 1 (1992).
13. R. Ramirez, M.F. Lapeña and J.A.Gonzalo, Ferroelectrics 124, 1 (1992).
14. B. Brezina and F. Smutny, Czech. J. Phys. B18, 1924 (1968).
15. A. J. Camnasio and J.A. Gonzalo, J. Phys. Soc. Jpn. 39, 451 (1975)
16. A. Camnasio and J.A.Gonzalo, Solid State Commun.16, 1169 (1975).
17. M. Koralewski, unpublished results (1987).